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(54) LASER IMAGABLE DRY PLANOGRAPHIC PRINTING PLATE

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ABSTRACT OF THE DISCLOSURE

A dry planographic printing plate which may be imaged by means of a laser beam, said plate comprising, on a lithographic substrate, a layer which is responsive to laser radiation and, overlying said layer, a layer of silicone rubber.

This invention relates to dry planographic printing plates.

Dry planographic printing plates are disclosed in United States Patent 3,677,178 granted July 18, 1972 and assigned to the assignee of the present invention. Such plates comprise a flexible substrate having coated thereon a cured solid but elastic silicone rubber film which will not remove conventional lithographic ink from an ink roller on a printing press.

Recently, methods have been proposed to utilize a laser beam to image a planographic (offset) or raised-image (letter press) printing plate, see for example United States Patent Nos. 3,506,779 granted April 14, 1970 (Brown et al.) "Laser Beam Type Setter" and 3,664,737 granted May 23, 1972 (Lipp) "Printing Plate Recording by Direct Exposure". While the laser offers great promise in producing high resolution printing plates, there has thus far been no practical way to image a dry planographic printing plate. The silicone rubber, which repels printing ink, is unaffected by laser radiation. The silicone rubber layer appears transparent to the energy and no significant reaction takes place. It might be possible to directly image a photosensitive dry planographic plate with a laser beam which emits light in the ultraviolet region. The disadvantage of such lasers is, however, that they are presently very expensive and do not have a high power output. In addition, such photosensitive plates would have to be handled under special, non-active lighting as overall exposure to ultraviolet would destroy their imaging capability. Furthermore, the shelf-life of any photosensitive coating is limited.

It is therefore of interest to provide a dry planographic printing plate which can be imaged by the use of a laser in a practical, commercially feasible manner.

According to this invention there is provided a dry planographic printing plate comprising, on an ink receptive substrate;

a laser responsive layer which contains particles which absorb laser energy, a self-oxidizing binder and a cross-linkable resin;

and

a film of silicone rubber overlying and in adherent contact with said layer.

With reference to the accompanying drawing:

Figure 1 is a cross-sectional view showing the construction of the dry planographic printing plate of the present invention;

Figure 2 is a cross-sectional view illustrating the formation of an image on the plate of the present invention.

The present invention provides a dry planographic printing plate comprising a laser responsive layer which contains particles which absorb laser energy, a self-oxidizing binder and a cross-linkable resin. In the preferred embodiment these energy absorbing particles are carbon particles and the self-oxidizing binder is nitrocellulose. The cross-linkable resin is preferably cross-linked by means of a cross-linking agent. As will be more fully illustrated hereinafter, the cross-linking reaction is conveniently initiated by heat. The laser responsive layer is interposed between a lithographic substrate and a film of silicone rubber. An image is recorded on the plate by writing with a laser in a conventional manner. Selected areas of the laser-responsive coating are loosened or removed by the laser beam so as to define an image on the plate.

The laser-responsive coating utilized in the present invention absorbs radiation in the infrared as well as the visible range. A suitable beam may be applied by YAG (yttrium-aluminum-garnet) laser which has an effective wave length of about 1.06 microns or by an argon laser beam which has an effective wave length in the range of from about 0.48 to about 0.52 micron. The beam of radiant energy is applied to the laser-responsive coating to loosen or vaporize and remove it and the overlying silicone rubber in selected areas so as to expose the underlying substrate.

In the areas irradiated by the laser the laser responsive

layer and the silicone rubber are removed, exposing the underlying lithographic substrate. The plate then accepts ink in the area struck by laser beam and repels ink in the non-image areas, as these areas are constituted by silicone rubber. The thus-imaged plate is subjected to an appropriate treatment, such as heating, to cross-link the resin in the remaining portions of the laser responsive layer, thereby forming a firm bond between the silicone rubber film and the underlying substrate and providing durable background areas on the planographic printing plate.

Referring now to the drawings, Fig. 1 depicts the composite structure of the article of the present invention. Substrate 10 may be a sheet of material conventionally used as a support for offset duplicating plates, e.g., metal, especially aluminum, paper or plastic. In the embodiment illustrated, the substrate 10 is aluminum. Since metals such as aluminum are so highly conductive of heat, in order to prevent the metal from dissipating the thermal energy provided by the laser, the substrate 10 is provided with an insulating layer 11 of an olephilic or ink receptive resin.

The composition of the resin for layer 11 is not critical, any of the oleophilic resins which are commonly used in the lithographic printing art and which provide good adhesion to the metal being suitable and the choice of such a resin is well within the skill of the worker in the art. Illustrative of the ink receptive resins suitable for use in the present invention include phenol- and cresol-formaldehyde resins especially the Novolak resins, urea formaldehyde resins, melamine-formaldehyde resins, vinyl resins, alkyd resins, polyester resins, polyacrylate including polymethacrylate and polyethylaqrylate resins, polyamides (nylon), polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, copolymers of styrene and butadiene and polyalkylene especially polyethylene. Insulating layer 11 may be applied to the substrate 10 by conventional coating techniques in the form of

an aqueous latex or organic solvent solution. Alternatively, the resin may be applied by extruding it in the molten form, a technique commonly referred to as "hot melt" extrusion. In some cases, a film of a resin such as polyethylene, polystyrene or polyvinyl acetate may be laminated to substrate 10.

Over the insulating layer 11 is applied laser-responsive layer 12 which comprises particles which absorb laser energy, such as carbon black, a self oxidizing binder, such as nitrocellulose and a cross-linkable resin, such as a "Novolak" resin in combination with a cross-linking agent. Over the laser-responsive layer 12 is applied a silicone rubber top coating 13. Not illustrated, but preferred to insure good adhesion between the laser-responsive layer and the silicone rubber top coating 13, is the application of a primer for silicone rubber such as polytetrabutyl titanate or polytetraisopropyl titanate.

When the laser-responsive layer 12 is struck by appropriate laser radiation, it oxidizes or burns. The products of combustion from the irradiated area of the laser responsive layer 12, being hot and at least partially gaseous, necessarily attempt to escape their confinement between layers 13 and 11. The result, as shown in Fig. 2, is that the silicone rubber overlying the irradiated area is either directly removed by the escaping products of combustion or the bond of the silicone rubber to the underlying layers is sufficiently weakened that it can later be removed by the application of a suitable developer solution.

After development, the imaged plate is subjected to a heat treatment of, for example, 400°F., for one-half minute to increase the adhesion of the silicone rubber remaining in the background areas, thus increasing run length of the plate.

EXAMPLE I

To a 3 mil. thick sheet of Mylar* polyester film was applied a laser responsive coating of the following composition:

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	Parts by Weight
Carbon black	15.4
Nitrocellulose (self-oxidizing)	7.7
"Novolak" resin (non-oxidizing cross-linkable resin)	60.9
Melamine derivative cross-linking agent ("Cymel"* 301 sold by American Cyanamid Co.)	15.4
P-toluene sulfonic acid (catalyst)	0.6

Methyl ethyl ketone in an amount sufficient to adjust total solids content to 20% by weight.

The coating composition was applied to the substrate using a No. 6 mayer rod and dried. The weight of the dry coating was 0.5 pounds per ream, (3,300 square feet).

Over this laser-responsive coating was applied a tie coat of polytetrabutyl titanate (DuPont "Tyzor"*PB) to enhance adhesion between the laser responsive coating and the subsequently applied silicone rubber. The tie coat was applied as a 4% organic solvent solution by a No. 6 mayer bar in a nominal amount of less than 0.1 pounds per ream (dry weight basis). Thereupon, a layer of silicone rubber ("Dow Corning 79-037 RTV")*was applied by No. 16 mayer rod in an amount of 3 pounds per ream (dry weight basis).

An image was etched into the plate by means of a YAG laser beam. The plate was developed by application of naphtha solvent to remove debris in the irradiated areas, leaving the polyester substrate exposed in the image areas.

The developed plate was mounted on an offset duplicating press without connecting the dampening system and yielded many satisfactory copies.

EXAMPLE II

To a 5 mil. thick sheet of aluminum provided with a coating of a cross-linked carboxy poly(vinyl benzal) resin (disclosed in United States Patent 3,776,888) was applied a laser responsive coating of the following composition:

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	Parts by Weight
Carbon black	10
Nitrocellulose (self-oxidizing)	5
"Novolak" resin (non-oxidizing)	50
Melamine derivative cross-linking agent ("Cymel"*301 sold by American Cyanamid Co.)	2.5
p-toluene sulfonic acid	0.1

Methyl ethyl ketone in an amount sufficient to adjust total solids content to 20% by weight.

The coating composition was applied to the substrate using a No. 4 mayer rod and dried. The weight of the dry coating was 0.65 pounds per ream, (3,300 square feet).

Over this laser-responsive coating was applied a tie coat of polytetrabutyl titanate (DuPont "Tyzor"* PB) to enhance adhesion between the laser-responsive coating and the subsequently applied silicone rubber. A tie coat was applied as a 4% organic solvent solution by a No. 5 mayer bar in a nominal amount of less than 0.1 pounds per ream (dry weight basis). Thereupon, a layer of silicone rubber ("Dow Corning 79-037 RTV")* was applied by No. 16 mayer rod in an amount of 3 pounds per ream (dry weight basis).

An image was etched into the plate by means of a YAG laser beam. The plate was developed by application of naphtha solvent to remove debris in the irradiated areas, leaving the coated aluminum substrate exposed in the image areas.

The developed plate was mounted on an offset duplicating press without connecting the dampening system and yielded many satisfactory copies.

While the invention has been particularly described with reference to preferred embodiments thereof, it is understood that various other changes and modifications thereof will occur to a person skilled in the art without departing from the spirit and scope of the invention as defined by the appended claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A laser-imageable dry planographic printing plate comprising:

an ink receptive substrate;

a film of silicone rubber overlying the substrate; and

a laser-responsive layer interposed between the film of silicone rubber and the substrate, and which is capable of being oxidized when irradiated with a laser beam to produce products of combustion which escape by selectively loosening or removing the overlying areas of the silicone rubber film, the laser-responsive layer comprising particles which absorbs laser energy, a self-oxidizing binder, and a cross-linkable resin for cross-linking after laser-imaging to form a firm bond between the unremoved portions of the silicone rubber film and the substrate.

2. A plate according to claim 1, wherein the substrate is metal provided with an insulating layer of oleophilic resin between the laser-responsive layer and the metal substrate to prevent the metal substrate from dissipating the thermal energy provided by the laser.

3. A plate according to claim 1 or 2, wherein the particles are carbon black.

4. A plate according to claim 1 or 2, wherein the self-oxidizing binder is nitrocellulose.

5. A plate according to claim 1 or 2, wherein the laser-responsive layer further includes a cross-linking agent.

6. A method of imaging a laser-imageable dry planographic printing plate comprising an ink receptive substrate, a film of silicone rubber overlying the substrate, and a laser-responsive layer interposed between the film of silicone rubber and the substrate and which is capable of being oxidized when radiated with a laser beam to produce products of combustion which escape by selectively loosening or removing the overlying areas of the silicone rubber film, the laser-responsive layer comprising particles which absorb laser energy, a self-oxidizing

binder and a cross-linkable resin for cross-linking after laser-imaging to form a firm bond between the unremoved portions of the silicone rubber film and the substrate, the method comprising the steps of:

(a) oxidizing the self-oxidizing binder in selected areas of the laser-responsive layer by directing a laser beam onto the selected areas to produce products of combustion which escape by loosening or removing the areas of silicone rubber film overlying the selected areas of the laser-responsive layer;

(b) developing the plate to completely remove the areas of silicone rubber film; and

(c) heating the imaged plate to cross-link the cross-linkable resin in the remaining laser-responsive layer to form a firm bond between the remaining silicone rubber film and the substrate.

7. A method according to claim 6, wherein the laser-responsive layer of the printing plate further includes a cross-linking agent.

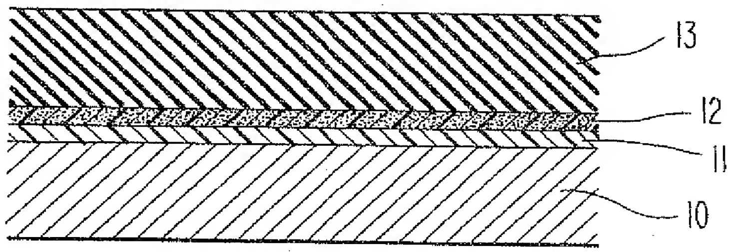

Fig. 1

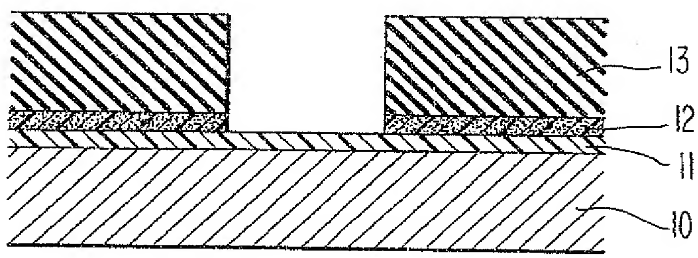

Fig. 2

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